

New Application Transmittal

Docket No.: 2543-28-93

Express Mail Mailing Label No.: EM062753093US

Date of Mailing: June 17, 1998



Assistant Commissioner for Patents
Patent Application
Washington, D.C. 20231

Transmitted herewith for filing is the patent application of

Inventors: Tod C. Duvall

For (title): SYNERGISTIC BLEND OF A METAL-BASED STABILIZER OR LEWIS ACID AND A FREE MERCAPTAN FOR ENHANCED PVC STABILIZER

Enclosed are:

1. **Benefit of Prior U.S. Application (35 U.S.C. 120)**
☒ The new application being transmitted claims the benefit of a prior U.S. application, and enclosed are added pages for new application transmittal where benefit of a prior U.S. application claimed.

2. **Papers Required For Filing Date Under 37 C.F.R. 1.53(b):**

18 Pages of Specification

01 Pages of Abstract

02 Pages of claims

00 Sheets of Drawing

☐ formal

☐ informal

In addition to the above papers, there is also attached:

Declaration or Oath

☒ Enclosed

☐ original

executed by (check all applicable boxes)

☒ inventor(s)

☐ legal representative of inventor(s). 37 CFR 1.42 or 1.43

☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.

☐ This is the petition required by 37 CFR 1.47 and the statement required by 37 CFR 1.47 is also attached.

See item 9 below for fee.

☐ Not Enclosed

☐ Application is made by a person authorized under 37 CFR 1.41(c) on behalf of all the above named inventor(s).

The declaration or oath, along with the surcharge required by 37 CFR 1.16(e) can be filed subsequently.

☐ Showing that the filing is authorized. (Not required unless called into question. 37 CFR 1.41(d).)

4. **Inventorship Statement**

The inventorship for all the claims in this application are:

☒ the same

OR

☐ are not the same and an explanation, including the ownership of the various claims at the time the last claimed invention was made, is submitted.

5. **Language**

☒ English

☐ Non-English

☐ A verified English translation of the

☐ specification and claims

☐ declaration

is attached.

6. **Assignment**
☒ An assignment of the invention to Morton International, Inc.
☒ is attached
☐ will follow

7. **Certified Copy**

(country) (appln. no.) (filed)

from which priority is claimed .

8. **Fee Calculation**

Claims as Filed					
	Number Filed		Number Extra	Rate	Basic Fee \$790.00
Total Claims	11	- 20 =	0	X \$22.00	\$0.00
Independent Claims	2	- 3 =	0	X \$82.00	\$0.00
Multiple Dependent claim(s), if any			0	+ \$270.00	\$0.00
TOTAL FEE DUE					\$790.00

- ☐ Amendment cancelling extra claims enclosed.
☐ Amendment deleting multiple dependencies enclosed.
☐ Fee for extra claims is not being paid at this time

9. **Fee Payment Being Made at This Time**

- ☐ Not Enclosed
☐ No filing fee is to be paid at this time. (This and the surcharge required by 37 CFR 1.16(e) can be paid subsequently.)

- ☒ Enclosed
☒ basic filing fee

\$790.00

- ☐ petition fee for filing by other than all the inventors or person on behalf of the inventor where inventor refused to sign or cannot be reached. (\$130.00; 37 CFR 1.47 and 1.17(h))

\$ 0.00

- ☐ for processing an application with a specification in a non-English language (\$130.00; 37 CFR 1.52(d) and 1.17(k) or 37 CFR 1.445(a)(6))

\$ 0.00

- ☐ processing and retention fee
(\$130.00; 37 CFR 1.53(b) and 1.21(l))

\$ 0.00

Total fees enclosed. \$790.00

10. **Method of Payment of Fees**

- ☐ check in the amount of \$ _____
- ☒ charge Account No. 13-4722 in the amount of \$790.00. A duplicate of this transmittal is attached.

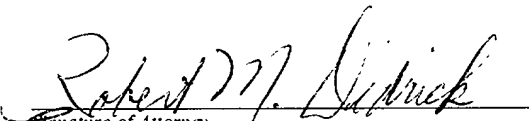
NOTE: Fees should be itemized in such a manner that it is clear for which purpose the fees are paid. 37 CFR 1.22(b).

11. **Authorization to Charge Additional Fees**

- ☒ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. 13-4722.
- ☒ 37 CFR 1.16 (filing fees)
- ☒ 37 CFR 1.16 (presentation of extra claims)
- ☒ 37 CFR 1.17 (application processing fees)
- ☐ 37 CFR 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 CFR 1.311(b)).

12. **Instructions as to Overpayment**

- ☒ credit Account No. 13-4722
- ☐ refund



Signature of Attorney

Robert M. Didrick
Reg. No. 25,135

Morton International, Inc.
100 North Riverside Plaza
Chicago, Illinois 60606-1596
Tel. No. (312) 807-2182

- ☒ Plus added page for new application transmittal where benefit of a prior U.S. application is claimed.

ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED**13. Benefits of Prior U.S. Application**

This application is a Continuation-In-Part of prior U.S. application

serial number 09/048,492, filed March 26, 1998; which is a C-I-P of U.S.S.N. 09/890,613, filed July 9, 1997; which is a C-I-P of U.S.S.N. 08/597,093, filed February 23, 1996; which is a C-I-P of U.S.S.N. 08/435,413, filed February 10, 1995.

International Application _____ filed _____ which designated the U.S.

14. Maintenance of Copendency of Prior Application

A petition, fee and response has been filed to extend the term in the pending prior application until

15. Conditional Petition for Extension of Time in Parent Application

☐ *A conditional petition for extension of time is being filed in the pending parent application.*

16. Relate Back - 35 U.S.C. 120

☒ *Amend the specification by inserting before the first line the sentence:*

This is a C-I-P of copending application serial number 09/048,492, filed on March 26, 1998; which is a C-I-P of U.S.S.N. 09/890,613, filed July 9, 1997; which is a C-I-P of U.S.S.N. 08/597,093, filed February 23, 1996; which is a C-I-P of U.S.S.N. 08/435,413, filed February 10, 1995..

☐ *International application _____ filed on _____ which designated the U.S.*

17. Abandonment of Prior Application (if applicable)

☐ *Please abandon the prior application at a time while the prior application is pending or when the petition for extension of time in that application is granted and when this application is granted a filing date so as to make this application copending with said prior application.*

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SYNERGISTIC BLEND OF A METAL-BASED STABILIZER OR
LEWIS ACID AND A FREE MERCAPTAN FOR ENHANCED PVC STABILIZATION

FIELD OF THE INVENTION

5 This invention relates to a heat stabilized halogen-
containing polymer composition normally susceptible to heat-
induced deterioration which comprises a free mercaptan in
combination with a very low level of a Lewis acid or metal-based
10 stabilizer. The combination is an excellent heat stabilizer when
used as the sole stabilizing additive in the polymer composition.
This invention relates particularly to the stabilization against
heat of vinyl chloride polymer compositions and to articles of
manufacture such as rigid pipe, flexible film and window profile
15 that are prepared from such heat-stabilized vinyl chloride
polymer compositions.

BACKGROUND OF THE INVENTION

20 It is well known that the physical properties of various
organic polymers deteriorate and color changes take place during
processing of the polymer and during exposure of formed polymer
products to certain environments. Halogen-containing polymers
are normally susceptible to heat-induced deterioration through
autoxidation. The prime examples of such polymers are the vinyl
25 polymers in which the halogen is attached directly to carbon
atoms. Poly(vinyl chloride) and copolymers of vinyl chloride and
vinyl acetate are the most familiar polymers which require

5 stabilization for their survival during fabrication into pipe,
window casings, siding, bottles, tubing, and the like. When such
polymers are processed at elevated temperatures, undesirable
color changes often occur within the first 5 to 10 minutes and
continue during later stages of the processing. Haziness, which
sometimes accompanies the color changes, is particularly
undesirable where clear products are needed. The addition of
heat stabilizers to such polymers has been absolutely essential
to the wide-spread utility of the polymers. From a great deal
10 of work in the development of more and more effective heat
stabilizers there has emerged two principal classes: organotin
compounds and mixed metal combinations. Organotin-based heat
stabilizers have been the most efficient and widely used
stabilizers for rigid PVC. Synergistic combinations of alkyltin
mercaptides and free mercaptans are particularly efficient heat
15 stabilizers for rigid PVC during extrusion. They have not been
entirely satisfactory, however, and are not typically used in
flexible PVC.

20 The stabilization of halogen-containing polymer compositions
normally susceptible to heat-induced deterioration by a
combination of a Lewis acid at a very low concentration and the
degradation products of a latent mercaptan during processing of
the polymer composition at an elevated temperature, which
products include a liberated mercaptan, is taught in co-pending,
25 commonly assigned patent application Serial No. 08/890,613, filed
July 9, 1997, which is incorporated herein by reference.

30 Although the combination of a latent mercaptan and a Lewis
acid is very beneficial because of the absence of offensive odor
and the oxidative stability of the latent mercaptan, the cost of
the latent mercaptan is not justified in certain applications
where an unblocked mercaptan would give satisfactory performance
in combination with a Lewis acid.

SUMMARY OF THE INVENTION

It is an object of this invention, therefore, to provide a cost competitive heat stabilizer for a halogen-containing polymer having the synergy of a metal-based stabilizer and/or Lewis acid with such a liberated mercaptan.

It is a related object of this invention to stabilize rigid, semi-rigid, and flexible PVC resin compositions with a heat stabilizer composition of this invention.

It is still another object of this invention to provide a flexible PVC composition and article stabilized against heat by a synergistic combination of a free mercaptan and a metal-based stabilizer and/or a Lewis acid.

These and other objects of the invention which will become apparent from the following description are achieved by adding a free mercaptan and a synergistic amount of a metal-based stabilizer and/or Lewis acid to a composition comprising a halogen-containing polymer before processing the composition at an elevated temperature.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, the term halogen-containing organic polymers as used herein means halogen-containing polymers or resins in which the halogen is attached directly to the carbon atoms. The halogen-containing polymers which can be stabilized according to this invention include chlorinated polyethylene having 14 to 75%, e.g. 27%, chlorine by weight, chlorinated natural and synthetic rubber, rubber hydrochloride, chlorinated polystyrene, chlorinated polyvinyl chloride, polyvinyl bromide, polyvinyl fluoride, and vinyl chloride polymers. PVC composition means a composition comprising a vinyl chloride polymer. As used herein, the term alkyl means a saturated monovalent straight or branched chain hydrocarbon radical containing from 1 to 20 carbon atoms. The term "free mercaptan" means a mercaptan which has not been liberated from a latent mercaptan during the PVC processing. The word "substantially" means largely if not wholly that which is specified but so close to it that the difference is inconsequential.

5 Metal-based stabilizers are defined for the purposes of this invention as being tin-free metal salts. For the purposes of this invention, metal salts are defined to include oxides, hydroxides, sulfides, sulfates, chlorides, bromides, fluorides, iodides, phosphates, phenates, perchlorates, carboxylates, and carbonates. The metal salt stabilizers are exemplified by zinc, barium, strontium, calcium, magnesium, cobalt, nickel, titanium, antimony, and aluminum salts of phenols, aromatic carboxylic acids, fatty acids, epoxidized fatty acids, oxalic acid, acetic acid, and carbonic acid. Calcium stearate, calcium 2-ethylhexanoate, calcium octanoate, calcium oleate, calcium ricinoleate, calcium myristate, calcium palmitate, calcium laurate, barium laurate, barium stearate, barium di(nonylphenolate), magnesium stearate, zinc octanoate (or caprylate), zinc 2-ethylhexanoate, zinc stearate, zinc laurate, zinc oxide, zinc hydroxide, zinc sulfide, and Group I and II metal soaps in general are examples of suitable salts along with aluminum stearate and hydrotalcite. The synergistic amount of the metal-based stabilizer is between about 0.01 and 0.5%, preferably 0.02-0.4%, and more preferably 0.03-0.1% by weight of the halogen containing resin. The zinc salts are much preferred because they provide not only dynamic stability to the heat processed resin but also superior color hold properties in comparison with the other metal salts, especially at very low concentrations such as from 0.03 to 0.1 %.

15 The Lewis acids are exemplified by boron trifluoride, aluminum chloride, zinc chloride and methyltin trichloride. The synergistic amounts of the Lewis acids for the purposes of this invention are between about 0.005 and 0.5%, preferably from about 0.01, more preferably from about 0.03, to about 0.1 % by weight of the halogen-containing resin. The Lewis acids and the metal-based stabilizers may be used in combination.

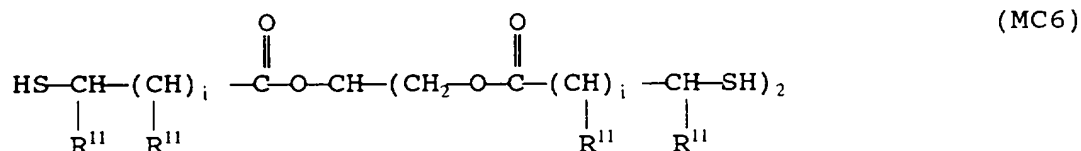
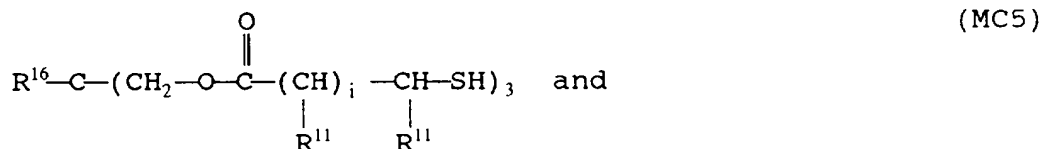
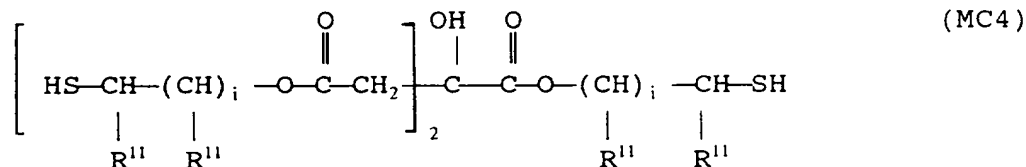
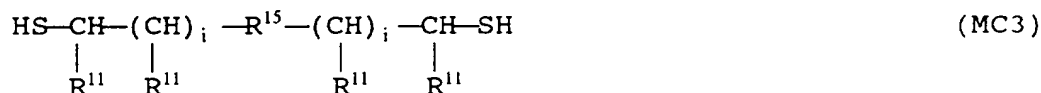
25 The vinyl chloride polymers are made from monomers consisting of vinyl chloride alone or a mixture of monomers comprising, preferably, at least about 70% by weight of vinyl chloride, based on the total monomer weight. Examples of the copolymers include those made from vinyl chloride and from about

1 to about 30% of a copolymerizable ethylenically unsaturated material such as vinyl acetate, vinyl butyrate, vinyl benzoate, vinylidene chloride, diethyl fumarate, diethyl maleate, other alkyl fumarates and maleates, vinyl propionate, methyl acrylate, 2-ethylhexyl acrylate, butyl acrylate and other alkyl acrylates, methyl methacrylate, ethyl methacrylate, butyl methacrylate and other alkyl methacrylates, methyl alpha-chloroacrylate, styrene, trichloroethylene, vinyl ethers such as vinyl ethyl ether, vinyl chloroethyl ether and vinyl phenyl ether, vinyl ketones such as vinyl methyl ketone and vinyl phenyl ketone, 1-fluoro-2-chloroethylene, acrylonitrile, chloroacrylonitrile, allylidene diacetate and chloroallylidene diacetate. Typical copolymers include vinyl chloride-vinyl acetate (96:4 sold commercially as VYNW), vinyl chloride-vinyl acetate (87:13), vinyl chloride-vinyl acetate-maleic anhydride (86:13:1), vinyl chloride-vinylidene chloride (95:5); vinyl chloride-diethyl fumarate (95:5), and vinyl chloride 2-ethylhexyl acrylate (80:20).

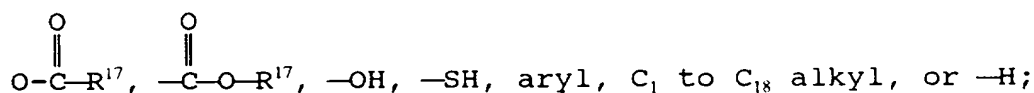
A rigid PVC composition of this invention is one which does not contain a plasticizer. A semi-rigid PVC composition of this invention is one which contains from 1 to about 25 parts of a plasticizer per 100 parts by weight of the vinyl chloride polymer. A flexible PVC composition of this invention contains from about 25 to about 100 parts of a conventional plasticizer per hundred parts of the vinyl chloride polymer. Alkyl esters of carboxylic acids in which there are from 1 to 3 alkyl groups having from 8 to 12 carbon atoms are representative of such plasticizers. The alkyl group may be n-octyl, 2-ethylhexyl, nonyl, decyl, or dodecyl. Suitable esters include phthalates, trimellitates, benzoates, adipates, glutarates, and sebacates. The plasticizer may also be a pentaerythritol or such an ester thereof. A polymeric plasticizer is also suitable.

The mercaptans that are suitable for the purposes of this invention are well-known compounds and include alkyl mercaptans, mercapto esters, mercapto alcohols, thioglycerols, and mercapto acids. See, for example, U.S. Patent Nos. 3,503,924 and 3,507,827, which are incorporated herein by reference. Alkyl

mercaptans having from 1 to about 200 carbon atoms and from 1 to 4 mercapto groups are suitable. Among the useful mercaptan-containing organic compounds are those having structures illustrated by the following formulas:



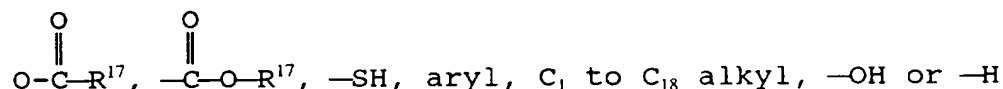
wherein R^{10} and R^{19} are the same or different and are



R^{11} is $-H$, aryl, or C_1 to C_{18} alkyl;

R^{12} is cycloalkyl, cycloalkenyl or phenyl;

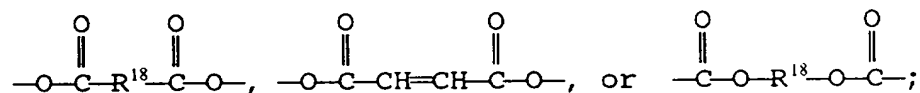
R^{13} is



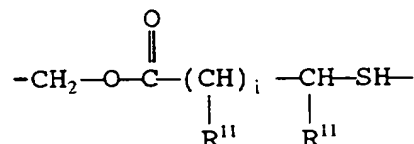
with the proviso that in formula (MC2) when R^{12} is phenyl, R^{13} is $-OH$ and $i=0$, then the $-SH$ groups are on non-adjacent carbon atoms;

R^{14} is $-H$ or a divalent group which may contain halogen, hydroxy, mercapto or alkyl substituents and which when R^{12} is phenyl combines with the phenyl to form a naphthalene ring;

R^{15} is

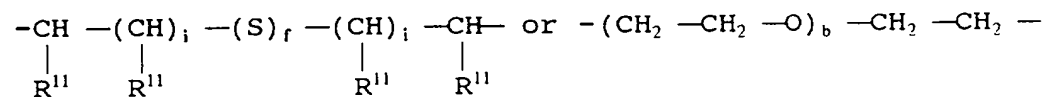


R^{16} is $-CH_3$, $-CH_2CH_3$, or



R^{17} is $-H$, or alkyl, alkenyl, aryl, aralkyl, alkaryl, cycloalkyl, cycloalkylenyl;

R^{18} is arylene, C_1 to C_8 alkylene, or



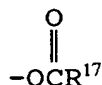
wherein b is an integer from 1 to 6;

$i=0$ or an integer from 1 to 6 inclusive;

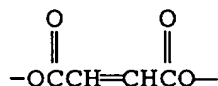
$j=0-4$; and

$f=1$ or 2.

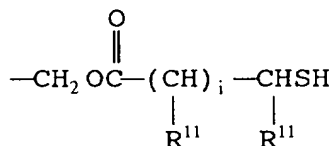
5 Mercaptan-containing organic compounds preferred in this invention are those compounds according to formula (MC1) where R^{11} is $-H$, R^{19} is $-H$, R^{10} is OH or



and $i=1$; those compounds according to formula (MC2) where R^{12} is phenyl, R^{11} is $-H$, R^{13} is $-H$, R^{14} is $-H$, $i=1$, and $j=1$; those compounds according to formula (MC3) where R^{11} is $-H$, R^{15} is

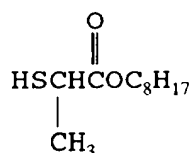
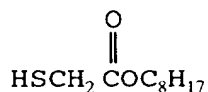
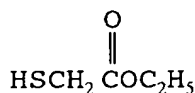
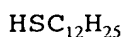


and $i=1$; those compounds according to formula (MC4) where R^{11} is $-H$ and $i=1$; those compounds according to formula (MC5) where R^{16} is $-C_2H_5$ or

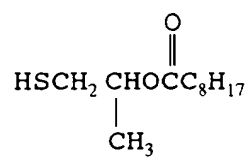


R^{11} is $-H$ and $i=0$ or 1 ; and those compounds according to formula (MC6) where R^{11} is $-H$ and $i=1$.

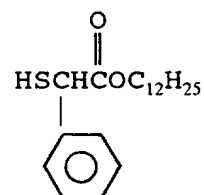
25 Examples of the mercaptan-containing organic compounds described by formula (MC1) include, but are not limited to, the following compounds:



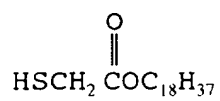
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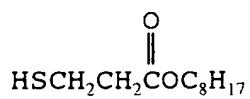
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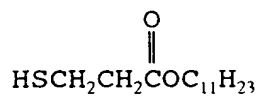
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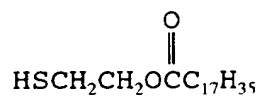
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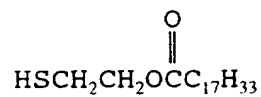
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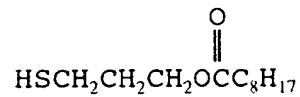
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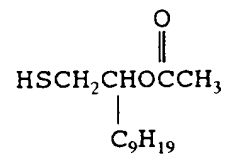
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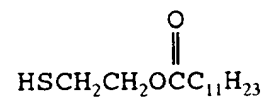


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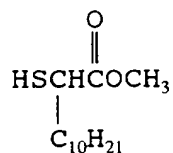


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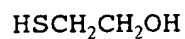
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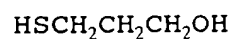
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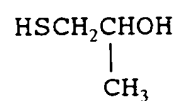
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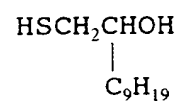
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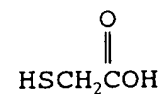
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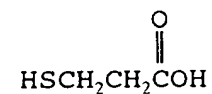
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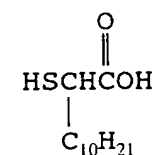
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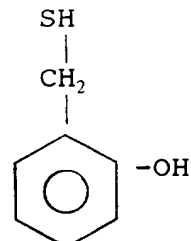
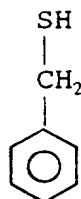
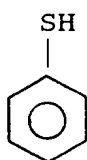


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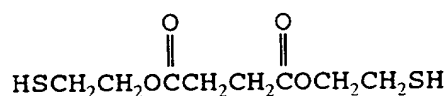
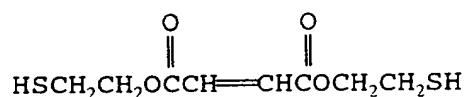
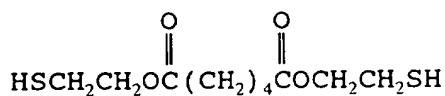
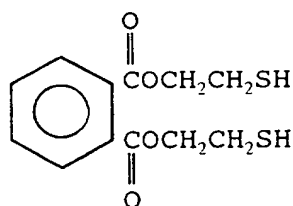
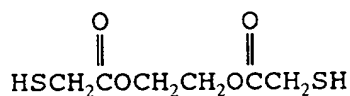


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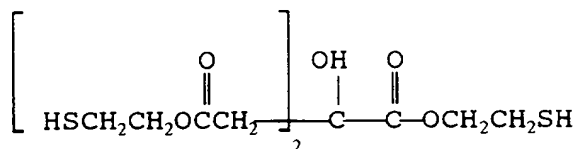
Examples of the mercaptan-containing organic compounds described by formula (MC2) include, but are not limited to, the following compounds:



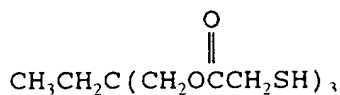
Examples of mercaptan-containing organic compounds represented by formula (MC3) include, but are not limited to the following compounds:



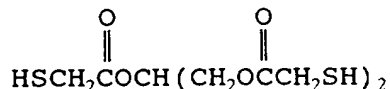
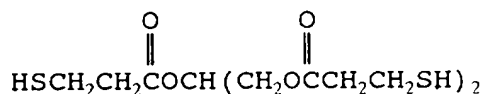
The mercaptan-containing organic compounds described by formula (MC4) are exemplified by, but are not limited to, the following:



The mercaptan-containing organic compounds represented by formula (MC5) are exemplified by, but are not limited to, the following:



The mercaptan-containing organic compounds represented by formula (MC6) are exemplified by, but are not limited to, the following:



The free mercaptans are employed in this invention in an amount sufficient to impart the desired resistance to heat deterioration to halogen-containing organic polymers. It will be readily apparent to one of ordinary skill in the art, that the precise amount of stabilizer composition used will depend upon several factors, including, but not limited to, the particular halogen-containing organic polymer employed, the temperature to which the polymer will be subjected, and the possible presence of other stabilizing compounds. In general, the more severe the conditions to which the halogen-containing organic polymer is subjected, and the longer the term required for resisting degradation, the greater will be the amount of stabilizer composition required. Generally, as little as about 0.10 part by weight of the free mercaptan per hundred parts by weight of the halogen-containing polymer will be effective. While there

is no critical upper limit to the amount of free mercaptan which can be employed, amounts of about 3.0 parts or less by weight per hundred parts of the polymer are preferred.

5 The synergistic amount of the metal-based stabilizer is between about 0.01 and 0.5%, preferably from about 0.01 to about 0.4%, and more preferably from about 0.03 to about 0.1% by weight of the halogen containing resin. The synergistic amount of the Lewis acids for the purposes of this invention is between about 0.005 and 0.5%, preferably from about 0.01, more preferably from
10 about 0.03, to about 0.1 % by weight of the halogen-containing resin. The zinc-based stabilizers (e.g., a carboxylate or the chloride) are much preferred because they provide not only dynamic stability to the heat processed resin but also superior color hold properties in comparison with the other stabilizers, especially at very low concentrations such as from 0.03 to 0.1 %.

The stabilizer compositions of this invention are particularly suited to impart superior stabilization against the deteriorative effects of heat and ultra-violet light on PVC
20 resins in comparison with stabilizer compositions previously known in the art. They consist essentially of from about 10 % to about 99 %, preferably from about 85 to about 97 %, by weight of free mercaptan, based on the total weight of the stabilizer composition, the balance comprising the metal-based stabilizer and/or Lewis acid. They may be prepared by blending the components thereof in any convenient manner which produces a homogeneous mixture, such as by shaking or stirring in a container. Likewise, the stabilizer compositions of this invention can be incorporated in semi-rigid and flexible PVC
30 resins by admixing the components of the stabilizer composition and of the resin composition, such as, for example, in an appropriate mill or mixer or by any other of the well-known methods which provide uniform distribution of the stabilizer throughout the resin composition.

35 Conventional non-metallic stabilizers and antioxidants can also be included in the PVC compositions of the present invention. Thus, there can be included 0.01-0.75 %, based on the

weight of the resin, of sulfur containing compounds such as dilauryl-thiodipropionate, distearyl 3,3'-thiodipropionate, dicyclohexyl-3,3-thiodipropionate, diolel-3,3'-thiodipropionate, dibenzyl-3,3'-thiodipropionate, didecyl-3,3'-thiodipropionate, 5 dibenzyl-3,3'-thiodipropionate, and diethyl-3,3'-thiopropionate.

An antioxidant may be added in an amount of 0.01-10%, preferably 0.1-5% by weight of the PVC resin. Phenolic antioxidants are particularly suitable and are exemplified by 2,6-di-t-butyl-p-cresol, butylated hydroxyanisole, propyl 10 gallate, 4,4'-thiobis(6-t-butyl-m-cresol), 4,4'-cyclohexylidene diphenol, 2,5-di-t-amyl hydroquinone, 4,4'-butylidene bis(6-t-butyl-m-cresol), hydroquinone monobenzyl ether, 2,2'-methylene-bis(4-methyl-6-t-butyl phenol), 2,6-butyl-4-decyloxy phenol, 2-t-butyl-4-dodecyloxy phenol, 15 2-t-butyl-4-dodecyloxy phenol, 2-t-butyl-4-octadecyloxy phenol, 4,4'-methylene-bis(2,6-di-t-butyl phenol), p-amino phenol, N-lauryloxy-p-amino phenol, 4,4'-thiobis(3-methyl-6-t-butyl phenol), bis [o-(1,1,3,3-tetramethyl butyl)phenol] sulfide, 4-acetyl- β -resorcylic acid, A-stage p-t-butylphenolformaldehyde 20 resin, 4-dodecyloxy-2-hydroxybenzophenone, 3-hydroxy-4-(phenylcarbonyl) phenyl palmitate, n-dodecyl ester of 3-hydroxy-4-(phenyl carbonyl) phenoxyacetic acid, and t-butyl phenol.

From 0.01-30% by weight of an epoxy compound, based on the 25 weight of the vinyl chloride polymer in the PVC compositions of this invention may also be used. Examples of such epoxy compounds include epoxidized soya bean oil, epoxidized lard oil, epoxidized olive oil, epoxidized linseed oil, epoxidized castor oil, epoxidized peanut oil, epoxidized corn oil, epoxidized tung 30 oil, epoxidized cottonseed oil, epichlorhydrin/bis-phenol A resins, phenoxy-propylene oxide, butoxypropylene oxide, epoxidized neopentylene oleate, glycidyl epoxystearate, epoxidized α -olefins, epoxidized glycidyl soyate, dicyclopentadiene dioxide, epoxidized butyl toluate, styrene 35 oxide, dipentene dioxide, glycidol, vinyl cyclo-hexene dioxide, glycidyl ether of resorcinol, glycidol ether of hydroquinone, glycidyl ether of 1,5-dihydroxynaphthalene, epoxidized linseed oil

fatty acids, allyl glycidyl ether, butyl glycidyl ether, cyclohexane oxide, 4-(2,3-epoxypropoxy) aceto-phenone, mesityl oxide epoxide, 2-ethyl-3-propyl glycidamide, glycidyl ethers of glycerine, pentaerythritol and sorbitol, and 3,4-epoxycyclohexane-1, 1-dimethanol bis-9,10-epoxystearate.

Likewise there can be used organic phosphites in an amount of 0.01 to 10%, preferably 0.1-5% by weight of the vinyl chloride polymer. The organic phosphites contain one or more, up to a total of three, aryl, alkyl, aralkyl and alkaryl groups, in any combination. The term "trialkylaryl" is inclusive of alkyl, aryl, alkaryl and aralkyl phosphites containing any assortment of alkyl, aryl, alkaryl and aralkyl groups. Exemplary are triphenyl phosphite, tricresyl phosphite, tri(dimethylphenyl) phosphite, tributyl phosphite, trioctyl phosphite, tridodecyl phosphite, octyl diphenyl phosphite, dioctyl phenyl phosphite, tri(octyl-phenyl) phosphite, tri(nonylphenyl) phosphite, tribenzyl phosphite, butyl dicresyl phosphite, octyl di(octyl-phenyl) phosphite, tri(2-ethyl-hexyl) phosphite, tritolyl phosphite, tri(2-cyclohexylphenyl) phosphite, tri-alpha-naphthyl phosphite, tri(phenylphenyl) phosphite, and tri(2-phenylethyl) phosphite.

Likewise there can be included from 0.01-10% by weight of the vinyl chloride polymer of a polyol stabilizer for vinyl chloride resins. Thus there can be included glycerol, sorbitol, pentaerythritol, mannitol, and polyethers such as diethylene glycol, triethylene glycol, tetraethylene glycol, tripropylene glycol, and the like.

Nitrogen containing stabilizers such as dicyandiamide, melamine, urea, formoguanamine, dimethyl hydantoin, guanidine, thio-urea, 2-phenylindoles, aminocrotonates, N-substituted maleimides, uracil, uracil derivatives such as the pyrrolodiazine diones described in published European Patent Application No. EP-736569 by Ciba-Geigy A.G., and the 1,3-dialkyl-6-amino-uracils described in German Offen. DE 19,741,778 by Ciba Specialty Chemicals Holding Inc., and the like also can be included in amounts of 0.1-10% by weight.

In addition to the stabilizers of this invention, the polymer compositions of this invention may contain conventional additives such as pigments, fillers, blowing agents, dyes, ultraviolet light absorbing agents, densifying agents, and lubricants such as low molecular weight polyethylene, i.e. polyethylene wax, fatty acid amides, e.g. lauramide and stearamide, bisamides, e.g. decamethylene, bis amide, and fatty acid esters, e.g. butyl stearate, glyceryl stearate, linseed oil, palm oil, decyloleate, corn oil, cottonseed oil, hydrogenated cottonseed oil, montan wax, stearic acid, calcium stearate, mineral oil, and oxidized polyethylene, etc.

The following examples further illustrate the preparation of stabilizer compositions of this invention, and the advantages of said stabilizer compositions.

EXAMPLE 1 and Comparative Example 1

In these examples, the stabilizing activity of the combination of a free mercaptan and a metal salt is compared with that of a combination of the same metal salt and a latent mercaptan known as 2-S-(tetrahydropyranyl)mercaptoethyltallate which is made by the addition of 2-mercaptoethyltallate to 3,4-dihydropyran. The amounts of the free mercaptan and of the latent mercaptan impart an equal sulfhydryl content to the examples. Accordingly, flexible PVC compositions containing:

<u>INGREDIENT</u>	<u>AMOUNT</u>
PVC resin (k=70)	100.0 parts
Diisodecyl phthalate	40.0 phr
Epoxidized soybean oil	5.0 "
Stearic acid	0.2 "
Oxidized polyethylene	0.2 "
Zinc octanote (18% Zn)	0.05 "

and either 1.7 phr of 2-mercaptoethyltallate (Example 1) or 2.0 phr of the latent mercaptan (Comparative Example 1) were processed using a Brabender PLASTICORDER rheometer at 200°C (392°F)/80rpm with chips taken at two minute intervals to a

maximum of 18 minutes. The color properties of the chips were measured using a Hunter Labs Colorimeter (L, a, b) and the dE was selected as the measurement for comparison in Table I.

TABLE I

PVC Color Hold (dE) Minutes									
Time\ Ex.	2	4	6	8	10	12	14	16	18
1	31.5	29.8	30.6	31.9	33.8	37.2	40.7	47.3	83.3
CE 1	30.7	31.2	31.6	32.6	34.8	38.3	41.6	44.1	77.6

EXAMPLES 2 and 3 and Comparative Example 2

In these examples, the flexible PVC compositions were the same as in Example 1 and CE 1 except that the plasticizer was dioctyl phthalate and equal weights (2 phr) of the free mercaptans and latent mercaptan were used and the free mercaptan in Example 2 is thioglycolic acid. The compositions were tested as in Example 1 except that the test was extended to 24 minutes. The results are given in Table 2.

Table 2

PVC Color Hold (dE) Minutes												
Time\ Ex.	2	4	6	8	10	12	14	16	18	20	22	24
2	25.7	25.8	25.7	26.4	26.6	28.6	29.8	31.2	34.0	35.9	37.8	44.6
3	26.1	26.1	26.9	28.0	29.4	30.6	32.2	33.2	34.4	35.5	38.6	39.5
CE2	26.3	25.9	26.7	27.7	29.2	30.6	32.4	32.7	33.6	33.9	34.0	54.3

EXAMPLE 4

In this example, the flexible PVC composition is the same as in Example 1 except that the zinc octanoate is replaced by zinc chloride.

Articles of manufacture contemplated by this invention, e.g., pipe, tubing, and window profile, are formed from the stabilized compositions of this invention by any of the well-known conventional techniques for forming polymers into shaped articles.

While a few specific embodiments of this invention have been disclosed in considerable detail, variations and modifications of these embodiments can be effected without departing from the spirit and scope of the invention as disclosed and claimed herein.

The subject matter claimed is:

1. A composition comprising a halogen-containing polymer, a free mercaptan and between about 0.005 and 0.5 %, based on the weight of the polymer, of at least one stabilizer selected from the group consisting of a metal-based stabilizer and a Lewis acid.
2. The composition of claim 1 wherein the amount is from about 0.01 to about 0.4%.
3. The composition of claim 1 wherein the amount is from about 0.03 to about 0.1%.
4. The composition of claim 1 wherein the Lewis acid is zinc chloride.
5. The composition of claim 1 wherein the stabilizer is a zinc carboxylate.
6. The composition of claim 1 wherein the halogen-containing polymer is a semi-rigid or flexible PVC.
7. The composition of claim 1 wherein the halogen-containing polymer is a rigid PVC.
8. The composition of claim 6 wherein the mercaptan is 2-mercaptoethyltallate.
9. The composition of claim 7 wherein the free mercaptan is thioglycolic acid.
10. A composition for stabilizing a halogen-containing polymer consisting essentially of from about 10 % to about 99% by weight of a free mercaptan and at least one stabilizer selected from the group consisting of a metal-based stabilizer and a Lewis acid as the remainder.

11. The composition of claim 10 wherein the stabilizer is zinc chloride.

ABSTRACT OF THE DISCLOSURE

Compositions comprising halogen-containing polymers such as PVC resins are stabilized against heat by a synergistic combination of a free mercaptan and a metal-based stabilizer and/or a Lewis acid such as zinc chloride.

S:\2543-93\PA254393 602

Combined Declaration and Power of Attorney

Attorney's Docket No.: 2543-28-93

(Original, Design, National Stage of PCT, Supplemental, Divisional, Continuation or CIP Application)

As a below named inventor, I hereby declare that:

Type of Application

This declaration is for the Original application:

Inventorship Identification

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

SYNERGISTIC BLEND OF A METAL-BASED STABILIZER OR LEWIS ACID AND A FREE MERCAPTAN FOR ENHANCED PVC STABILIZATION

Specification Identification

the specification of which:

- a) ☒ is attached hereto.
- b) ☐ was filed on _____ as application Serial No. _____ and was amended on _____ (if applicable).
- c) ☐ was described and claimed in PCT International Application No. _____ filed on _____ and as amended under PCT Article 19 on _____ (if any).

Acknowledgements of Review of Papers and Duty of Candor

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Patent and Trademark Office all information known to the inventor to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

☐ In compliance with this duty there is attached an information disclosure statement. 37 CFR 1.97.

Priority Claim

I hereby claim foreign priority benefits under Title 35, United States Code Section 119, of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international applications(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

- d) ☒ no such applications have been filed.
- e) ☐ such applications have been filed as follows:

Earliest foreign application(s), if any, filed within 12 months
(6 months for design) prior to this U.S. application.

Country	Application Number	Date of Filing (month, day, year)	Priority	Claimed
			Under 37	USC 119
			Yes	No
			Yes	No
			Yes	No
			Yes	No
			Yes	No

All foreign application(s), if any, filed more than 12 months
(6 months for design) prior to U.S. application

Power of Attorney

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

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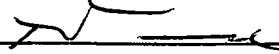
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Declaration

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signatures

Type or print full name of sole or first inventor Tod C. Duvall

Inventor's signature 

Date: 6-8-94 Country of Citizenship: USA

Residence: 7692 Whitehall Circle, West Chester, OH 45069

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Type or print name of second joint inventor, if any _____

Inventor's signature _____

Date: _____ Country of Citizenship: _____

Residence: _____

Post Office Address: SAME

Type or print full name of third joint inventor, if any _____

Inventor's signature: _____

Date: _____ Country of Citizenship _____

Residence: _____

Post Office Address: SAME

Type or print full name of fourth inventor, if any _____

Inventor's signature _____

Date: _____ Country of Citizenship: _____

Residence: _____

Post Office Address: SAME

Type or print full name of fifth joint inventor, if any _____

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ADDED PAGE TO COMBINED DECLARATION AND POWER OF ATTORNEY
FOR DIVISIONAL, CONTINUATION OR CIP APPLICATION

PATENT
2543-28-93

Claim for benefit of earlier U.S./PCT application(s) under 35 U.S.C. 120

Page 4 of 4

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application.

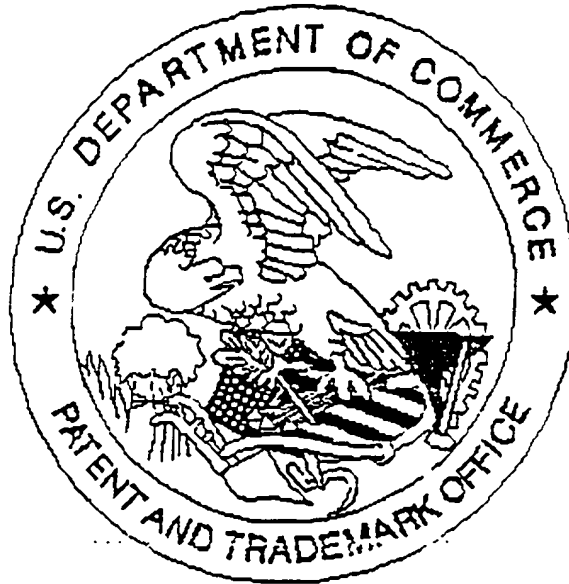
Prior U.S. Applications or PCT International Applications Designating the U.S. for benefit under 35 USC 120:					
U.S. Applications			Status (Check one)		
U.S. Applications	U.S. Filing Date	Patented	Pending	Abandoned	
1. 09/048,492	March 26, 1998		X		
2. 09/890,613	July 9, 1997		X		
3. 08/597,093	February 23, 1996		X		
4. 08/435,413	February 10, 1995		X		
5.					
6.					
7.					
PCT Applications Designating the U.S.					
PCT Application No.	PCT Filing Date	U.S. Serial Nos. Assigned (if any)			
8.					
9.					
10.					

35 USC 119 Priority Claim, if any, for above listed U.S./PCT Applications

Above Application No.	Details of Foreign Application from which priority claimed under 35 USC 119		
	Country	Application No.	Date of Filing (month, day, year)
1.			
2.			
3.			
4.			
5.			
6.			

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